

Quantum Tunneling and Quantum-Classical Transitions in Large Spin Systems

Bambi Hu^{1,2}, De-gang Zhang^{1,3}, and Bo-zang Li⁴

¹*Department of Physics and Centre for Nonlinear Studies, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China*

²*Department of Physics, University of Houston, Houston, TX 77204, USA*

³*Institute of Solid State Physics, Sichuan Normal University, Chengdu 610068, China*

⁴*Institute of Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100080, China*

We have studied quantum tunneling of large spins in a biaxial spin system and in a single-axial spin system with a transverse magnetic field. The asymptotically exact eigenvalues and eigenstates of the spin systems are obtained by solving the Mathieu equation. When the height $4q$ of energy barrier formed by the anisotropy and the magnetic field exceeds some critical values $4q_{1T}(r)$, the ground states and the excited states split due to tunneling of large spins. We also have presented the phase diagram of these spin systems in the extremely weak spin-phonon coupling limit. The crossover from thermal to quantum regime is second order. With further decreasing temperature, the first order phase transition occurs from a thermally-assisted resonant tunneling to thermal regime as $q < q_{1T}(s)$. Our theory agrees with recent experimental observations well.

PACS number(s): 75.10.Jm, 73.40.Gk, 75.60.Jp, 03.65.Db

In recent years quantum tunneling of magnetization (QTM) in small magnetic particles has been widely investigated in both theory and experiment because of its fundamental interest in exploring the transition between classical and quantum physics [1]. It gives evidence of quantum mechanical behavior in macroscopic systems. Such phenomena have been observed experimentally in ferritin [2], the molecular nanomagnets $\text{Mn}_{12}\text{-ac}$ [1, 3, 4], Fe_8 [5, 6], BaFeCoTiO [7], etc at very low temperatures. Theoretical calculations of such effects were performed for the ferromagnets [1, 8] and antiferromagnets without and with the excess spin [1, 9] by using path integral and WKB methods, etc.. However, these approaches depend on the semiclassical treatment and did not present the energy spectrum of the spin systems, which is necessary to give the complete solutions of spin tunneling problems. Especially, the quantization of spin levels becomes very important to explain well the experiments of quantum tunneling at very low temperatures [4]. In very recent Refs. [10-12], the spin systems arouse new interest again because they provide examples exhibiting first order phase transitions, which were not known previously. The energy spectrum of the spin systems can also help us to understand the origin of the first order phase transition. In this paper, we investigate a biaxial spin system without the magnetic field and a single-axial spin system with a transverse magnetic field which are generic for spin tunneling problems studied by different methods [1, 8, 10-12] in the framework of the Schrödinger's picture of quantum mechanics, so that the energy spectrum as well as the physical properties of the spin systems are obtained.

We first consider QTM in the biaxial spin system without the magnetic field described by the Hamiltonian [1,

8, 11]

$$H = AS_z^2 - BS_x^2, \quad (1)$$

where the anisotropy constants A and B are taken to be positive. So the ground state of the system corresponds to spin \mathbf{S} pointing the positive or negative x axis. To diagonalize the Hamiltonian (1), we first write its matrix representation in the basis $|s, m\rangle$, which has the properties: $\mathbf{S}^2|s, m\rangle = s(s+1)|s, m\rangle$, $S_z|s, m\rangle = m|s, m\rangle$ and $S_{\pm}|s, m\rangle \equiv (S_x \pm iS_y)|s, m\rangle = \sqrt{s(s+1) - m(m \pm 1)}|s, m \pm 1\rangle$, where s is the spin quantum number to be taken as an integer [13], $m = -s, -s+1, \dots, s$ and the unit of $\hbar = 1$ is used. Let E and Ψ_m be the eigenenergies and the eigenstates of H , respectively, then we have

$$\begin{aligned} & \sqrt{[s(s+1) - (m-1)^2]^2 - (m-1)^2} \Psi_{m-2} \\ & + \sqrt{[s(s+1) - (m+1)^2]^2 - (m+1)^2} \Psi_{m+2} \\ & + 4\left[\frac{E}{B} + \frac{1}{2}s(s+1) - (\lambda + \frac{1}{2})m^2\right] \Psi_m = 0, \end{aligned} \quad (2)$$

where $\lambda = \frac{A}{B}$. For a large spin system, s is a sufficiently large number, i.e. $s \gg 1$. Define $\Phi_m = (-1)^{[\frac{m}{2}]} \Psi_m$, where $[\frac{m}{2}]$ denotes the integer part of $\frac{m}{2}$, then Eq. (2) becomes

$$(1-x^2) \frac{d^2\Phi}{dx^2} - 2x \frac{d\Phi}{dx} + \left[-\frac{E}{B} - \frac{1}{4} + \lambda s(s+1)x^2 - \frac{1}{4} \frac{1}{1-x^2}\right] \Phi = 0 \quad (3)$$

in the large- s limit. Here $x = \frac{m}{\sqrt{s(s+1)}}$ and only the leading terms are remained. Taking the transformations $\Phi = (1-x^2)^{-\frac{1}{4}} y(x)$ and $x = \sin t$ and substituting them into Eq. (3), we finally obtain the well-known Mathieu equation

$$\frac{d^2y}{dt^2} + [\Lambda(q) - 2q \cos(2t)]y = 0, \quad (4)$$

which describes the motion of a particle with the mass $\frac{1}{2}$ in the cosine potential. Here the characteristic values $\Lambda(q) = -\frac{E}{B} + 2q$ and $q = \frac{1}{4}\lambda s(s+1)$. Obviously, when $q = 0$, $\Lambda_{|m|}(0) = m^2$, then $E_m = -Bm^2$, which are the exact eigenenergies of (1) in the eigenstates $|s, m\rangle_x$. Now we have completed the mapping of the spin problem onto a particle problem. The energy spectrum of the Hamiltonian (1) is determined completely by the Mathieu equation.

The Mathieu equation (4) has been studied in a large set of literature [14, 15] due to its physically basic importance. It is known that there exist periodic solutions of period $n\pi$, where n is any positive integer. However, the solutions relative to quantum tunneling problem discussed here are only those even and odd ones with periods π and 2π , i.e., $y = ce_r(t, q)$ and $se_r(t, q)$, $r = 0, 1, \dots, s$. Assume that a_r and b_r are the characteristic values associated with the even and odd periodic solutions, respectively, then these characteristic values form a countable sequence, i.e. $a_0 < b_1 < a_1 < b_2 < a_2 < \dots < b_s < a_s$ for $q > 0$ and $a_{2i}(-q) = a_{2i}(q)$, $b_{2i}(-q) = b_{2i}(q)$, $a_{2i+1}(-q) = b_{2i+1}(q)$ and $b_{2i+1}(-q) = a_{2i+1}(q)$. We note that the approximately degenerate characteristic levels (a_r, b_r) are lifted remarkably as the energy barrier parameter q exceeds the critical value $q_{1T}(r)$. The higher the characteristic level is, the larger the critical value is, i.e. $q_{1T}(i) > q_{1T}(j)$ for $i > j$. The value of $q_{1T}(r)$ can be estimated by letting the height of the energy barrier be equal to the energy $\Lambda_r(0)$ of the particle in the vanishing energy barrier, i.e. $4q_{1T}(r) = r^2$, which is a good approximation for large r . This shows clearly that when $q > q_{1T}(r)$, the splitting of the characteristic levels (a_r, b_r) is induced by *tunneling* of the particle. As q is larger than $q_{2T}(r) \approx \frac{[s(s+1)]^2}{4(s-r+1)^2}$ [16], the levels b_r and a_{r-1} degenerate approximately due to very high energy barrier. Therefore, in order to observe experimentally tunneling splitting of level r , q must locate between $q_{1T}(r)$ and $q_{2T}(r)$. We also note that tunneling of the particle mainly occurs in those characteristic levels ranging from the highest level to one with characteristic value $a_s - s^2 + 0(s)$ as $q < q_{1T}(s)$, which is important to evaluating approximately the critical temperature from thermal to quantum regime below.

For the Hamiltonian (1), its lower excited states correspond to the higher characteristic levels of the Mathieu equation. In order to see the tunneling splitting of the degenerate ground states, q must exceed the critical value $q_{1T}(s) \approx \frac{1}{4}s^2$, i.e. $\lambda_{1T}(s) \approx 1 - \frac{1}{s}$, which coincides with the result reported previously [11] when s is very large. When $q > q_{2T}(m)$, we obtain tunneling splitting of the ground states as well as the excited states [14]

$$\Delta E_m = B(a_m - b_m) = B(2\sqrt{\lambda s(s+1)} - m) + 0(q^{-\frac{1}{2}}). \quad (5)$$

When $q \rightarrow \infty$, the ground state a_s is singlet while all the excited states are twofold degenerate, which coincide

with the degeneracy of the Hamiltonian (1) with $B \rightarrow 0$.

Our another example is devoted to the single-axial spin system with a transverse magnetic field, which Hamiltonian has form [1, 8, 10]

$$H = -hS_z - BS_x^2, \quad (6)$$

where $B > 0$ and $h > 0$. The Hamiltonian (6) can be also diagonalized by the same method mentioned above. Its energy spectrum is determined by the Mathieu equation (4), too. However, in this case, $x = \cos(2t)$, $\Lambda(q) = -\frac{4E}{B}$ and $q = \frac{2h\sqrt{s(s+1)}}{B}$. As $h = 0$, then $\Lambda_r(0) = r^2$ and $E_m = -Bm^2$. So the ground states and the excited states of the Hamiltonian (6) correspond to the characteristic levels (a_{2s}, b_{2s}) and (a_{2r}, b_{2r}) ($r < s$), respectively. According to that $4q_{1T}(m) = (2m)^2$, we have the critical magnetic field $h_{1T}(m) = \frac{Bm^2}{2\sqrt{s(s+1)}}$, $m \gg 1$. As $q < h_{1T}(m)$, there is no tunneling between the approximately degenerate energy levels E_m (i. e. a_{2m} and b_{2m}) of the Hamiltonian (6). As $h > h_{1T}(s) = \frac{Bs^2}{2\sqrt{s(s+1)}}$, the ground states occur splitting, which is the same with that in Ref. [10] for very large s . We also note that h must be smaller than $h_c = 2Bs$, at which the degenerate ground states coincide. As $q \gg 1$, we have

$$\Delta E_m = \frac{1}{4}B(a_{2m} - b_{2m}) = B\left(\sqrt{\frac{2h\sqrt{s(s+1)}}{B}} - \frac{1}{2}m\right) + 0(q^{-\frac{1}{2}}). \quad (7)$$

When $q \rightarrow \infty$, all the energy levels a_{2m} and b_{2m} are singlet, which agree with the energy spectrum of the Hamiltonian (6) with $B \rightarrow 0$. Because there is no Kramers' degeneracy in the Hamiltonian (6), tunneling splitting also holds for half odd integer spin s [14].

Up to now, we have constructed the energy spectrum of the pure spin systems (1) and (6). However, the experiments of observing quantum tunneling were performed at low temperatures. So the influence of phonons or thermal activation on tunneling must be considered. Here, we assume the spin-phonon coupling is so weak that the energy spectrum of the spin systems is not changed too much. The transition between the ground state and the excited states can be completed by absorbing or emitting phonons. With the help of the Debye theory of a solid [17], we obtain approximately the critical temperature T_c satisfying

$$3k_B T_c D\left(\frac{T_c}{\theta}\right) \approx Bs^2 \quad (8)$$

as $q < q_{1T}(s)$ and

$$\begin{aligned} 3k_B T_c D\left(\frac{T_c}{\theta}\right) &\approx B(a_s - b_r) & \text{for (1)} \\ &\approx \frac{1}{4}B(a_{2s} - b_{2r}) & \text{for (6)} \end{aligned} \quad (9)$$

as $q_{2T}(r) \leq q \leq q_{2T}(r+1)$ and $q_{2T}(2r) \leq q \leq q_{2T}(2r+1)$, respectively. Here the Debye function $D(x) \approx \frac{1}{5}\pi^4 x^3$ at

low temperature, k_B and θ are the Boltzmann constant and the Debye temperature, respectively. Obviously, the crossover from the high temperature (thermal) phase to the low temperature (quantum) phase is second order because tunneling splitting of large spin continuously transforms into zero. As $q < q_{1T}(s)$, in order to see tunneling, large spin must absorb at least energy $B(s^2 - 4q)$ and $B(s^2 - q)$ for the models (1) and (6), respectively, provided mainly by phonons or thermal activation. So we have the first order phase transition temperature T_0 ,

$$\begin{aligned} 3k_B T_0 D(\frac{T_0}{\theta}) &\approx B(s^2 - 4q) \text{ for (1).} \\ &\approx B(s^2 - q) \text{ for (6).} \end{aligned} \quad (10)$$

The phase diagram of the spin systems (1) and (6) is shown in Fig. 1.

Here we compare our theoretical results with recent experiments of quantum tunneling. The Hamiltonian (1) is believed to be a good description for the molecular nanomagnet Fe_8 with spin $s = 10$ [5]. The parameters $A = 0.092\text{K}$ and $B = 0.224\text{K}$, then $q = 11.295 < q_{1T}(s) = 25$. Therefore, with decreasing temperature, the spin system enters the thermally-assisted resonant tunneling regime II from thermal regime I, as observed down to 0.067K . However, tunneling can not be seen possibly if the temperature is further lowered to below T_0 , which would be of interest to be verified experimentally. The Hamiltonian (6) has been found to be a good approximation for the molecular nanomagnet $\text{Mn}_{12}\text{-ac}$ with spin $s = 10$ [4]. For this nanomagnet, $B = 0.68\text{K}$, then $h_{1T}(s) = 3.24\text{K}$. The parameter $h = g_{\perp}\mu_B H$ was changed from 6.38K to 8.93K in experiment, i.e. the magnetic field H was applied between 5T and 7T . So the spin system fell into quantum regime III, where the two states of the fundamental doublet of the high-spin molecule are lifted. The transitions between the two states induced by a two-phonon process have been observed from 0.1K to 0.02K when $H = 6.06\text{T}$ [4]. Obviously, as the spin systems just set in the thermal regime IV or $q > q_{2T}(s)$, tunneling does not be observed in experiments even at very low temperatures [18].

In summary, we have investigated quantum tunneling of large spins based on simple models (1) and (6). The asymptotically exact spectrum of the spin systems is completely determined in the full range of the magnetic anisotropy and the magnetic field. The degeneracy of all the energy levels is removed due to QTM. The phase diagram presented here coincides with the experimental observations. To our knowledge, the thermal regime IV in Fig. 2 was not predicted by previous theories. We think that the first order phase transition is not limited to the spin systems (1) and (6) and also exists generally in other spin systems, depending on whether the energy barrier and the ground states as well as the low-lying excited states cross. The method of solving the spin Hamiltonians used above is also applied to the other large spin systems, such as the other symmetric ferromagnets, antiferromagnets and etc., which is in progress.

This work is supported in part by grants from the Hong Kong Research Grants Council (RGC), the Hong Kong Baptist University Faculty Research Grant (FRG), the Sichuan Youth Science and Technology Foundation, the NSF of the Sichuan Educational Commission and the NSF of China (No. 19677101).

-
- [1] *Quantum Tunneling of the Magnetization*, edited by L. Gunther and B. Barbara, NATO ASI, Ser. E, Vol. 301 (Kluwer, Dordrecht, 1995); Bo-zang Li and Wen-ding Zhong, in *Aspects of Modern Magnetism* (F. C. Pu et al eds., World Sci., Singapore, 1996)57.
 - [2] D. D. Awschalom, J. Smyth, G. Grinstein, D. DiVincenzo, and D. Loss, Phys. Rev. Lett. **68**, 3092 (1992); J. Tejada, X. X. Zhang, E. del Barco, J. M. Hernández, and E. M. Chudnovsky, Phys. Rev. Lett. **79**, 1754 (1997).
 - [3] C. Paulsen, J. G. Park, B. Barara, R. Sessoli, and A. Caneschi, J. Magn. Magn. Mater. **140-144**, 379 (1995); J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996); S. Hill, J. A. A. J. Perenboom, N. S. Dalal, T. Hathaway, T. Stalcup, and J. S. Brooks, Phys. Rev. Lett. **80**, 2453 (1998).
 - [4] G. Bellessa, N. Vernier, B. Barbara, and D. Gatteschi, Phys. Rev. Lett. **83**, 416 (1999).
 - [5] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).
 - [6] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. **82**, 3903 (1999).
 - [7] W. Wernsdorfer, E. Bonet Orozco, K. Hasselbach, A. Benoit, D. Mailly, O. Kubo, H. Nakano, and B. Barara, Phys. Rev. Lett. **79**, 4014 (1997).
 - [8] J. L. Van Hemmen and A. Sütö, Physica **141**, 37 (1986); M. Enz and R. Schilling, J. Phys. C **19**, L711 (1986); E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988); G.-H Kim and D. S. Hwang, Phys. Rev. B **55**, 8918 (1997).
 - [9] B. Barbara and E. M. Chudnovsky, Phys. Lett. A **145**, 205 (1990); I. V. Krive and O. B. Zaslavskii, J. Phys: Cond. Matter. **2**, 9457 (1990); A. Chiolero and D. Loss, Phys. Rev. B **56**, 738 (1997); S. E. Barnes, R. Ballou, B. Barbara, and J. Strelén, Phys. Rev. Lett. **79**, 289 (1997).
 - [10] E. M. Chudnovsky and D. A. Garanin, Phys. Rev. Lett. **79**, 4469 (1997).
 - [11] J. -Q. Liang, H. J. W. Muller-Kirsten, D. K. Park, and F. Zimmerschied, Phys. Rev. Lett. **81**, 216 (1998).
 - [12] D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **56**, 11102 (1997); D. A. Garanin, X. Martinez Hidalgo and E. M. Chudnovsky, Phys. Rev. B **57**, 13639 (1998); D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **59**, 3671 (1999); Gwang-Hee Kim, Phys. Rev. B **59**, 11847 (1999); E. M. Chudnovsky, Phys. Rev. A **46**, 8011 (1992).
 - [13] For half odd integer spins, tunneling splitting of all the energy levels of the Hamiltonian (1) vanishes due to Kramers' degeneracy.

- [14] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, (New York: Dover, 1965).
- [15] J. Meixner and F. W. Schäfke, *Mathieusche Funktionen und Sphäroidfunktionen*, (Springer, Berlin, 1954).
- [16] The values of $q_{2T}(r)$ can be obtained by diagonalizing the Hamiltonian (1) in the basis $|s, m\rangle_x$, which also leads the Mathieu equation. $q_{1T}(r)$ and $q_{2T}(r)$ coexist.
- [17] C. Kittel, *Introduction to Solid State Physics*, 7th ed. (Wiley, New York, 1996).
- [18] W. Wernsdorfer, E. Bonet Orozco, K. Hasselbach, A. Benoit, B. Barbara, N. Demoncy, A. Loiseau, H. pascard, and D. Mailly, Phys. Rev. Lett. **78**, 1791 (1997).

FIG. 1. The phase diagram of the spin systems (1) and (6): I and IV are the thermal regimes; II is the thermally-assisted resonant tunneling regime; III is the quantum tunneling regime. The transition from I to II and III is second order while the transition from II to IV is first order.

Fig. 1

